

HYDROGEN PRODUCTION THROUGH SODIUM BOROHYDRIDE ETHANOLYSIS

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Abstract

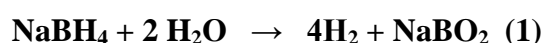
In this work, sodium borohydride (SB) ethanolysis was explored for the first time as a method to generate hydrogen for Polymer Exchange Membrane Fuel Cells. Ethanolysis by-product was characterized by [Fourier Transform Infrared Spectroscopy](#), [X-Ray Diffraction](#), and [Nuclear Magnetic Resonance](#). Metal and acid catalysts were tested. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was the best metal catalyst. Acetic acid was selected for the study because of its effectiveness, low cost and relative greenness. The maximum gravimetric hydrogen density obtained was 2.1 % wt. The addition of water produces an increase in hydrogen generation rate and a decrease in conversion. [The use of ethanol-methanol mixtures produces an increase in reaction rates in absence of catalyst](#). As a proof of concept the reaction was performed in a small reactor which operates by the addition of ethanolic acetic acid solutions to solid SB (in the form of granules). The reactor produces stable and constant hydrogen generation in the range of 20-80ml.min⁻¹ during 1h at constant temperature (around 27-35°C).

Keywords

Hydrogen production, sodium borohydride, ethanolysis , (bio)-ethanol, catalyst

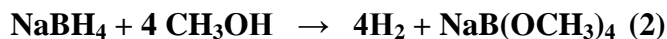
1.Introduction

At present, hydrogen is being considered as a clean energy carrier that may contribute to reduce the dependence on fossil fuels and the greenhouse effect produced by their use. Hydrogen has a high energy density (39.4 kWh.kg^{-1} while for hydrocarbons is 13.1 kWh.kg^{-1}) and its reaction with oxygen produces energy and water as only by-product. However, the use of hydrogen faces many challenges related to clean production, transport, storage and combustion (direct or in a fuel cell). Regarding hydrogen storage, great efforts have been made in these years to develop suitable materials with high gravimetric and volumetric density. Boron based hydrides are very attractive because of the combination of their lightweight and high hydrogen content [1-3]. Among them, sodium borohydride (NaBH_4 , SB) is the most studied because of its stability in dry air and safe handling [4-6]. Although it is no longer recommended for vehicular use, it still has potential for portable and niche applications [5]. SB produces hydrogen through catalysed solvolysis reactions. Sodium borohydride hydrolysis (reaction 1) is the most studied solvolytic reaction and has a potential gravimetric hydrogen density (GHD) around 10.8 % wt. Reaction (1) has demonstrated to be versatile enough to produce hydrogen in reactors in a wide range of rates ($0\text{-}6 \text{ L.min}^{-1}$) and with interesting effective GHDs (up to 9 wt% when employing solid SB and around 4 wt% when using stabilized SB solutions) [4-12].



As an alternative to the use of water, alcohols have been proposed as efficient solvolytic agents. In particular, methanolysis (reaction of SB with methanol, CH_3OH) has been reported (2) as advantageous because its high potential gravimetric hydrogen density

(GHD 4.9 wt%), the possibility of sub-zero hydrogen generation, and the fact that the reaction product ($\text{NaB}(\text{OCH}_3)_4$) does not have tendency to plug the reactors as occurs with NaBO_2 [13-20]. At present, some energy technologies that aim at using methanol are under development.



Recently, ethyleneglycol ($\text{OHCH}_2\text{CH}_2\text{OH}$) was reported as solvolytic agent, which, in combination with water, produced hydrogen at low temperatures with a 4.2 % wt experimental GHD [21-22].

Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) is another possible solvolytic agent for SB. It can be produced by bio-sources (bioethanol) thus reducing the dependence on petrochemical resources. Ethanolysis of sodium borohydride (3) would potentially combine the advantages of the use of alcohols (sub-zero hydrogen generation, non-sticky reaction by-products) with safety and green production. However, SB ethanolysis has been reported as very slow and the weight of ethanol is higher than that of methanol, reducing the gravimetric hydrogen density of the system. The potential GHD of this reaction (3) is 3.6 % wt, which is similar to the highest effective GHD previously reported for SB methanolysis (3.4 % wt) [15]. For this reason, in this paper sodium borohydride ethanolysis (3) was explored for the first time as a means of generating hydrogen to supply Polymer Exchange Membrane Fuel Cell (PEMFC).



Potential accelerators for reaction (3) were studied. Reaction product was characterized. The conditions to obtain the maximum GHD together with the behavior of the reaction using ethanol-water and ethanol-methanol mixtures was also studied and discussed.

The performance of the reaction was tested and discussed in a simple homemade device to produce hydrogen for PEMFCs.

2.Experimental

SB (powder 99% and granular 98%), metal salts, organic acids and cationic resins (Amberlyst® and DOWEX 50Wx8) were purchased from Sigma-Aldrich. Ethanol was purchased from Merck (99.9%, HPLC grade). All reagents were used as received.

For testing powder catalysts, 38mg of NaBH_4 were suspended in 1ml ethanol, and added to the powder catalyst (5mg) placed at the bottom of a closed three necked heart-shaped flask. For testing liquid catalyst (acetic acid), 38mg of NaBH_4 were placed at the bottom of the same flask and 1ml of acetic acid in ethanol (5mg acid /ml ethanol or the indicated concentration) was added.

The flask was immersed in a water bath maintained at $(25 \pm 0,5)^\circ\text{C}$ and connected to a 100 ml gas burette. The amount of evolved hydrogen was measured by reading the displacement of a piston (gas-tight by a mercury o-ring) as a function of time. No stirring was used for the experiments, except for the stirring effect of the evolved hydrogen. The hydrogen generation rate ($\text{ml} \cdot \text{min}^{-1}$) or ($\text{ml} \cdot \text{min}^{-1} \cdot \text{g}_{\text{catalyst}}^{-1}$) was obtained from the hydrogen evolution curves. R_{50} is the reaction rate calculated at 50% SB conversion. Total conversion (TC, %) was calculated using stoichiometry of reaction (3). Experiments were done at least twice, and showed to be reproducible within 5% experimental error.

Fourier Transform Infrared Spectroscopy (FTIR) measurements were collected in vacuum in a Fourier Transform spectrometer (JASCO.FT/IR 6200) on a KBr pellet. X-ray diffraction (XRD) measurements were performed using $\text{Cu K}\alpha$ radiation in an X-Pert Pro diffractometer using a PIXcel detector in the 2θ angle range of 5-50 degrees.

Sample was loaded in a capillary tube in a N₂ filled glovebox. Nuclear Magnetic Resonance (NMR) was also used for characterization of the reaction product. ¹H and ¹³C NMR spectra were recorded in dimethyl sulfoxide ((CH₃)₂SO, DMSO) on a Bruker Avance DRX-400 at 400MHz using the solvent as internal standard for calibration (2.5 ppm for ¹H, and 39.52 ppm for ¹³C). Carbon and hydrogen content was measured in the reaction product using a LECO TruSpec CHN analyzer.

3. Results and Discussion

3.1. Study of the reaction

Uncatalysed, SB ethanolysis is very slow. Figure 1 shows the corresponding hydrogen evolution curve. Ethanolysis by-product was recovered by filtering, washing with ethanol and distilled pentane and dried in vacuum. Figure 2.a shows the FTIR spectrum which was compared to that of sodium borate, ethanol and sodium borohydride. The broad band at 3351 cm⁻¹ is indicative of O-H stretching which can be assigned either to water (which also shows a peak 1617 cm⁻¹ corresponding to its bending mode), ethanol or both. C-H stretching bands at 2971, 2923, 2878, C-O stretching band at 1051 cm⁻¹ and B-O bands at 1380, 998 and 1270 cm⁻¹ (stretching and deformation respectively) confirm the presence of NaB(OCH₂CH₃)₄. XRD pattern was collected and is shown in Figure 2.b. Despite the crystalline structure of the NaB(OCH₂CH₃)₄ (obtained by reaction of NaBO₂ with ethanol) was reported previously, no reference XRD pattern was found in literature to compare [23]. For this reason, ¹H and ¹³C RMN spectra were measured in DMSO and results are shown as supporting information (Fig. 1S). Both spectra confirm the presence of NaB(OCH₂CH₃)₄ in accordance to previous report (¹H NMR: 3.24ppm, quartet; 0.97ppm triplet and ¹³C NMR: 54.5ppm ; 18.6ppm) [24]. The presence of 2 wt% free ethanol was also detected. Elemental Analysis was also

performed giving a 45.3 wt% C and 9.8 wt% H, also in agreement with the theoretical formula of $\text{NaB}(\text{OCH}_2\text{CH}_3)_4$, within the experimental error.

Metal salts, organic acids and cationic resins were tested as accelerators for reaction (3). Table 1 summarizes the results. As an example, Figure 1 shows the hydrogen evolution curves of metal and acid catalysed SB ethanolysis in comparison to the uncatalysed reaction. In these conditions, conversion was lower than 100% for all catalysts tested. Metal salts produced a black solid upon addition of ethanolic sodium borohydride. These black solids correspond to metal and/or metal-boron alloys reported for the first time by Schlesinger [25]. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ has shown the best efficiency followed by hydrated and anhydrous CoCl_2 salts. The rest of the tested salts (including H_2PtCl_6 and $\text{Pd}(\text{NO}_3)_2$) have shown less than 50% conversion in our experimental conditions. For metal catalysed ethanolysis, H_2 evolution curves can be divided into two phases: a phase I with non-linear H_2 evolution (in which metal salts convert into metal or metal-boron alloys) and a phase II with linear (zero-order in SB) H_2 generation (Fig. S.2, supplied as supporting information). The black solid resulting of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ -catalysed SB ethanolysis was isolated and tested for reaction (3). The solid is denoted as Co-B/Co because its nature is still under discussion [26]. Figure 1 shows that the performance of the Co-B/Co catalyst is significantly lower than that of CoCl_2 salts. The reusability of metal salts would not be advantageous because their activity decreases considerably after the first use. Similar trend was found for $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and Ru-B/Ru (not shown).

Among acidic accelerators, hydrochloric acid has shown the best performance followed by acetic and citric acid. Ascorbic and tartaric (the latter poorly soluble in ethanol) acid together with cationic resins have shown a conversion in the range of 40-55 %. Cationic

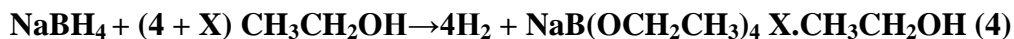
resins showed similar performance than the latter. The hydrogen evolution curves for acidic accelerators show a positive order (> 0) in SB.

Taking into account the cost of ruthenium salt and the low feasibility to reuse it with high activity, its use was disregarded in this study. As concerns to acidic accelerators, hydrochloric acid has shown higher rates but lower conversion respect to acetic acid. For this reason and its relative greenness, acetic acid was chosen as accelerator for further studies [27].

Figure 3.a shows the hydrogen evolution curves for the acetic acid catalysed SB ethanolysis with variable amounts of accelerator (3-9 mg acetic acid in 1ml ethanol). The inset plots the r_{50} as a function of the mass of catalyst. Activity was calculated from the slope as $2800\text{ml}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$. Conversion increases with the amount of acetic acid. Hydrogen evolution curve for 5mg of acetic acid was analysed using nth-order integrated equations. Results are presented in Fig .S.3 (as supporting information). None of the reaction orders in SB proposed (0, 1, 1.5 and 2) fitted the kinetics of the reaction during the whole experiment. Curves from Fig.3.a. were analysed using the equations proposed by Kaufman and Sen in previous work [28]. Results are shown in Tables S.1 and S.2 and Figure S.4 (as supporting information), and indicate dependence in H^+ concentration as a function of time in these conditions. A full kinetic analysis would require the use of buffer solutions or pH measurements during the experiments. However, such analysis is far from the scope of the present work.

For portable applications, it is desirable to achieve the conditions which ensures that the experimental gravimetric hydrogen density (GHD) remains as high as possible. In the conditions in which above tests were performed, (38mg SB + 1ml ethanol) the effective

GHD is 1% wt provided that 100% conversion is achieved. To find out the highest achievable GHD for SB ethanolysis, several tests were conducted with decreasing amounts of in ethanol (184, 276, 368 and 736 mg which corresponds to X= 0, 2, 4, 8 in equation 4) added to 38mg of SB (keeping constant the mass of acid in each experiment equal to 5mg)



Hydrogen evolution curves for the acetic acid catalysed ethanolysis as a function of X value are shown in Figure 3.b. Reaction rates increase with the amount of ethanol, suggesting a positive reaction order in ethanol. Table 2 shows the experimental GHD obtained in each case. It is shown that the reduction on the amount of ethanol produces an increase in the effective GHD from 0.9 (X= 8 excess of ethanol) to 2.1% wt for X=2. However, further decrease in the amount of ethanol (X=0, stoichiometric amount as suggested by (3)) also produces a decrease in total conversion, thus reducing the experimental value of GHD. In conditions of X= 4, 2, 0 a white precipitate appears at the end of the reaction. The same tests were performed for the citric acid and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ catalysed reaction (3) with similar results (maximum GHD_{exp} 1.9-2.2 wt%) indicating that this effect is independent of the nature of the catalyst. For both methanolysis (2) and hydrolysis (1), it was reported that the formation of solvated by-products (methanolated $\text{NaB}(\text{OCH}_3)_4$ and hydrated NaBO_2 , both solvent-consuming reactions) reduces the effective GHD respect to the theoretical [8,15,19]. Results obtained for the catalysed SB ethanolysis for X=0, suggest similar behaviour for the reaction product ($\text{NaB}(\text{OCH}_2\text{CH}_3)_4$).

One potential advantage of the system SB/ethanol as hydrogen producing reaction is the possibility to use a green hydrogen source of hydrogen such as bioethanol. This bioethanol could contain some amounts of water depending of the purification steps

performed. After fermentation process to produce bioethanol, the mixture can have up to 10% ethanol which is enriched to azeotropic point by distillation. Pure bioethanol is produced by extractive distillation of the azeotrope [29]. For this reason the effect of water addition in SB ethanolysis was studied. Several experiments were conducted by adding 1ml of ethanol-water (95:5, 70:30, 50:50 and 0 % v/v) mixture containing 5mg acetic acid to the same amount of SB. Figure 4.a. shows the results. Except for the 95:5 % v/v mixture, the addition of water accelerates the reaction up to 50-60% conversion, but then rates decrease respect to pure ethanol and pure water. For ethanol/water mixtures, solvolysis seems to occur through a hydrolytic pathway. Total conversion also decreases with the addition of water, being the effect more pronounced for the 95:5 %v/v ethanol/ water mixture (with 40% total conversion vs 90% for pure ethanol in same conditions). For this mixture, the formation of a precipitate at the beginning of the reaction could be responsible for low reaction rate and conversion. In the conditions of this work, the kinetics of acetic acid catalysed ethanolysis is not much slower than hydrolysis. Figure 4.a. also shows the kinetics of hydrogen production by methanolysis (reaction 2) with same amounts of acetic acid. The rate order in our conditions follows the well-known general trend: methanolysis >>hydrolysis> ethanolysis [15]. Ethanol/methanol (v/v %) mixtures were also tested as solvolytic agents in absence of any catalyst (Fig.4.b). As expected, the more methanol the faster the reaction

3.2. Practical applications

As a proof of concept, to test the possibility to produce hydrogen through SB ethanolysis for practical applications, a small single-use system was used (Figure 5). The system is a modification of one previously used for SB hydrolysis [30]. It consists of a small reactor (cylindric, 10ml) which loads granular SB (2g in each experiment).

Acetic acid was used as catalyst for its activity-conversion relationship and its relative greenness [27]. Ethanolic acetic acid solutions were added to the reactor through a pump ($1\text{ml}\cdot\text{min}^{-1}$). Reaction products were separated from the hydrogen produced in a gas-liquid separator, which is connected to a solvent adsorbent cartridge and then to a flowmeter. Reaction temperature was measured at the end of the reactor.

Figure 5.a. shows the hydrogen generation rate (HGR) as a function of time obtained for different concentrations of acetic acid (0.01-0.25 %v/v) during 1h. Hydrogen generation rates are constant in the range of $20\text{-}80\text{ ml}\cdot\text{min}^{-1}$ with constant temperature in the range of $27\text{-}35^{\circ}\text{C}$, both variables increasing with acid concentration. More concentrated solutions of acetic acid were tested (up to 1% v/v), but reaction rates were not as stable. As the experiments were conducted during a fixed time (60 min) for a fixed amount of SB, total conversion depends on the final HGR achieved. When 0.25% v/v acetic acid was employed, $75\text{-}80\text{ ml}\cdot\text{min}^{-1}$ hydrogen flow was obtained with a total conversion of 83% and a 0.9 % wt GHD.

Figure 5.b shows the HGR and temperature vs time plot for the 0.05 % v/v acetic acid solution pumped during 140min. Hydrogen generation rate remained stable during 100 min at around $20\text{ml}\cdot\text{min}^{-1}$ and then decreased to reach $12.5\text{ml}\cdot\text{min}^{-1}$ hydrogen flow after 140 min operation. Temperature was constant and around 27°C during the whole experiment.

To get an approximate idea of the achievable power level by this system, it was assumed that for a PEMFC operating at 0.7V, $1\text{g}\cdot\text{min}^{-1}\text{ H}_2$ is equivalent to 1125W [15]. For our system, the achievable power level is in the range 2-8W, adequate for small scale applications. Further investigation should be conducted to increase GHD of the system by finding the experimental conditions to obtain higher SB conversion with minimum amount of reactants.

4. Conclusions

In this paper, SB ethanolysis was studied for the first time as a method to produce hydrogen for PEMFC. This reaction combines the possibility of sub-zero hydrogen generation, the formation of non-sticky reaction by-products (both characteristics of alcoholysis reactions) with the low toxicity of ethanol. Furthermore, the solvolytic agent can be obtained from bio-sources (bio-ethanol). Acetic acid has shown the best compromise between hydrogen generation rates, conversion (increasing with the amount of accelerator) and greenness. The maximum experimental GHD obtained was 2.1 % wt. The addition of water to ethanol increases hydrogen rates but decreases conversion. The use of ethanol-methanol mixtures in absence of any catalyst increases reaction rates. A system was used to produce hydrogen through SB ethanolysis for PEMFC. The obtained hydrogen generation rates are adequate for small scale portable applications. The system has demonstrated to be able to produce stable hydrogen flow and temperature in the range of 20-80 ml.min⁻¹ and 27-35°C respectively during 1h, by varying acid concentration. In the best conditions maximum conversion achieved was 83%. The system would have potential in hydrogen storage-generation for portable application provided that conversion is optimized.

5. References

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FIGURE CAPTIONS

Figure 1. Hydrogen evolution curves for the metal and acid catalyzed SB ethanolysis in comparison to the uncatalysed reaction

Figure 2. (a) IR spectrum and (b) XRD pattern of the solid recovered for the uncatalysed SB ethanolysis.

Figure 3. Acetic acid as accelerator for SB ethanolysis. (a) Hydrogen evolution curves as a function of the mass of acid (inset: reaction rate, r_{50} as a function of the mass of catalyst). (b) Optimization of gravimetric capacity. Hydrogen evolution curves for the catalyzed ethanolysis as a function of the excess of ethanol (X) added.

Figure 4. (a) Acetic acid-catalysed SB ethanolysis for ethanol-water (v/v%) mixtures, in comparison to SB acetic-catalysed methanolysis. (b) Hydrogen evolution curves for ethanol-methanol mixtures (v/v%), in absence of any catalyst.

Figure 5. Experiments with granular SB in the reactor. (a) Hydrogen generation rate as a function of time for different acetic acid concentration. (b) Hydrogen generation rate and temperature as a function of time for 0.05% v/v acetic acid in ethanol.

TABLE LEGENDS

Table 1. Catalysts for SB ethanolysis. Total conversion and r_{50} for catalyzed SB ethanolysis for the different accelerators tested.

Table 2. Optimization of gravimetric capacity. Results obtained for the acetic acid catalyzed ethanolysis as a function of the excess (X) of ethanol added.

Table

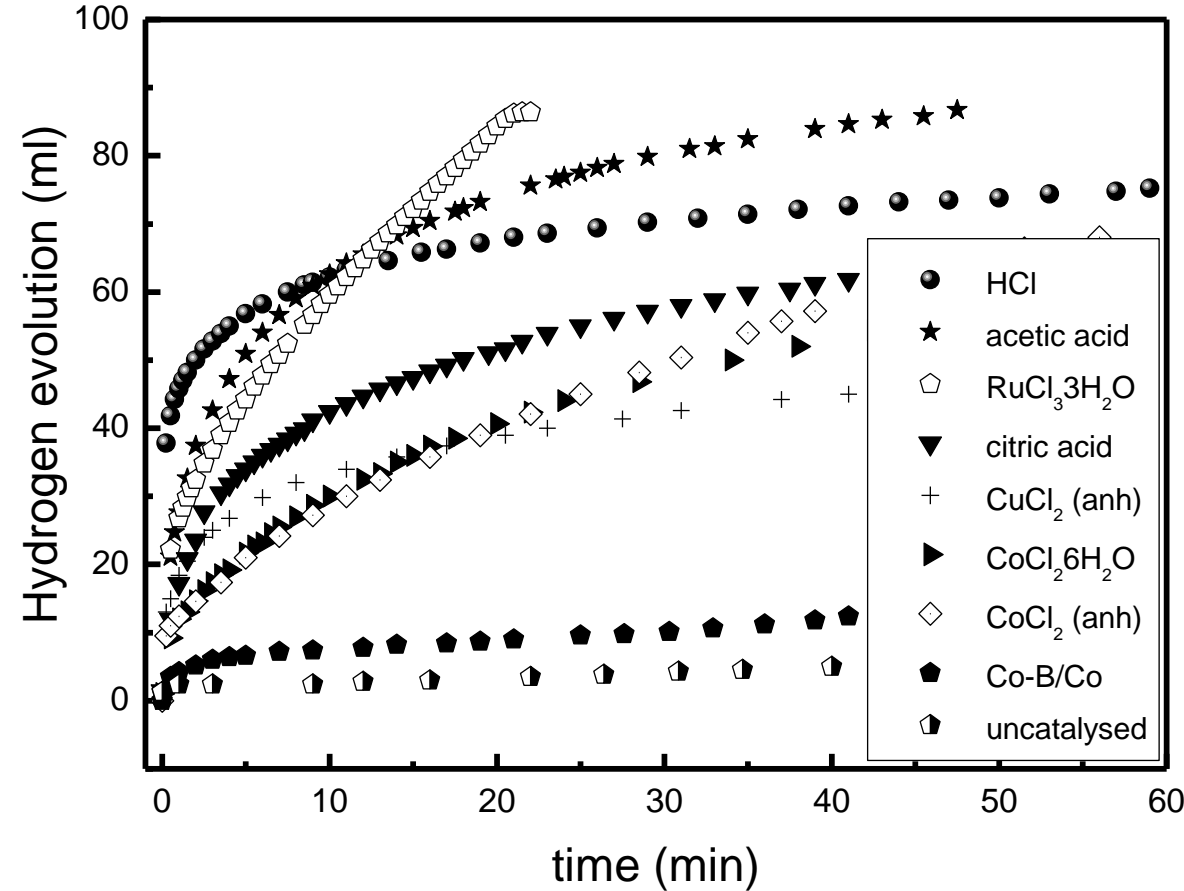
Metal catalyst	r_{50} (ml.min ⁻¹ .g ⁻¹)	Total conversion (%)	Acidic accelerators	r_{50} (ml.min ⁻¹ .g ⁻¹)	Total conversion (%)
RuCl ₃ .3H ₂ O	1450	89	HCl	5020	77
CoCl ₂ (anh)	320	72	Acetic	2000	90
CoCl ₂ .6H ₂ O	289	51	Citric	460	80
CuCl ₂ (anh)	-----	46	Ftalic	400	71
H ₂ PtCl ₆ .6H ₂ O	----	43	Boric	360	72
Co/Co-B	-----	38	Ascorbic	--	43
CuCl ₂ .2H ₂ O	-----	37	Tartaric	----	43
Pd (NO ₃) ₂	-----	30	Amberlyst ®	120	53
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Table

X	r_{50} (ml.min ⁻¹ .g ⁻¹)	TC %	GHD _{exp} [%]
0	590	60	2.1
2	1170	81	2.1
4	1480	87	1.7
8	2000	90	0.9

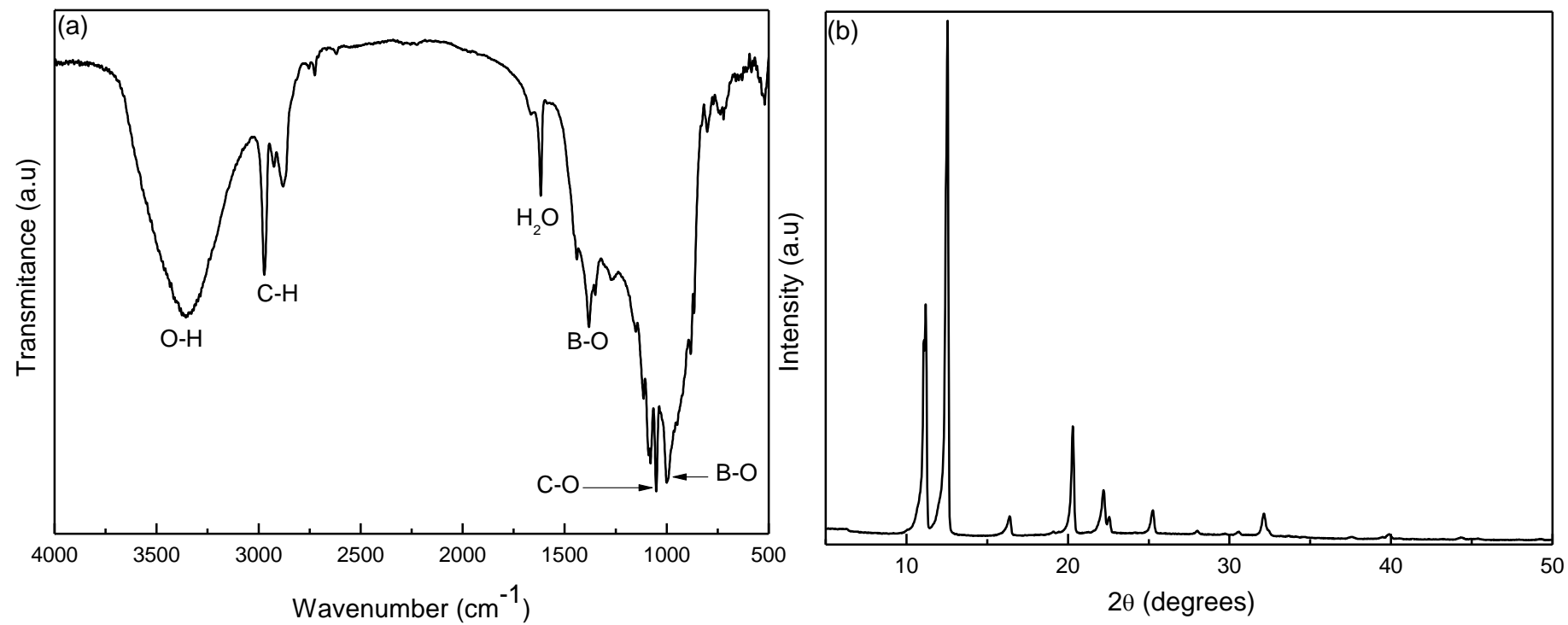
Figure

Figure 1



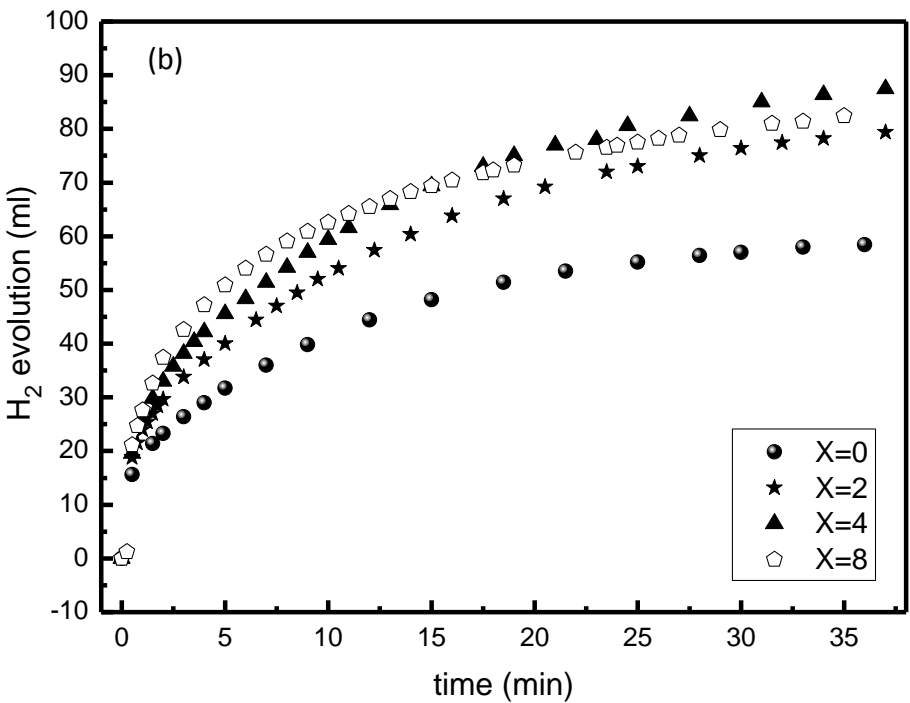
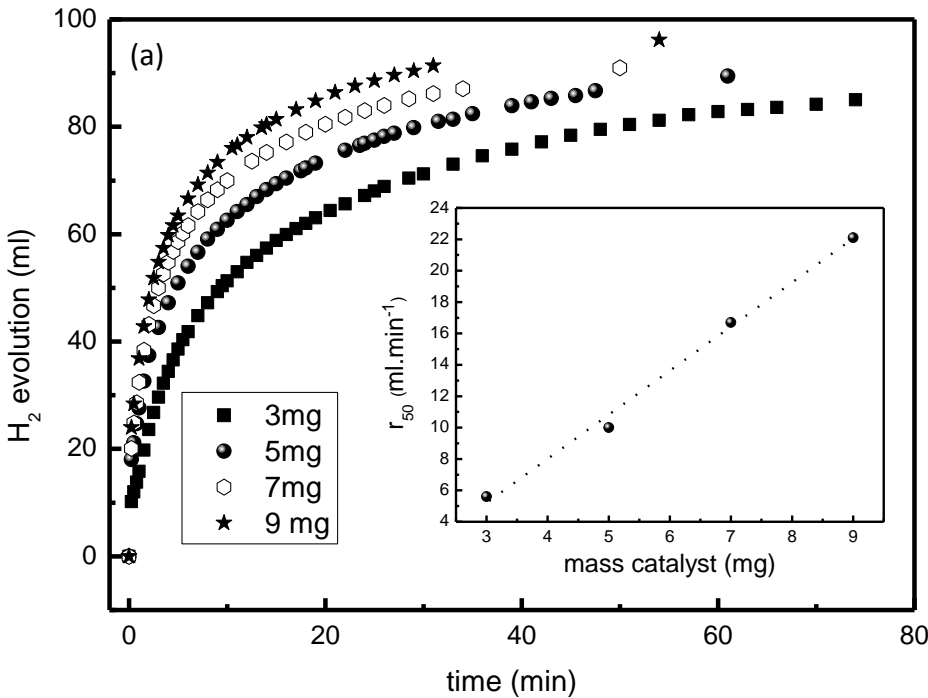
Figure

Figure 2



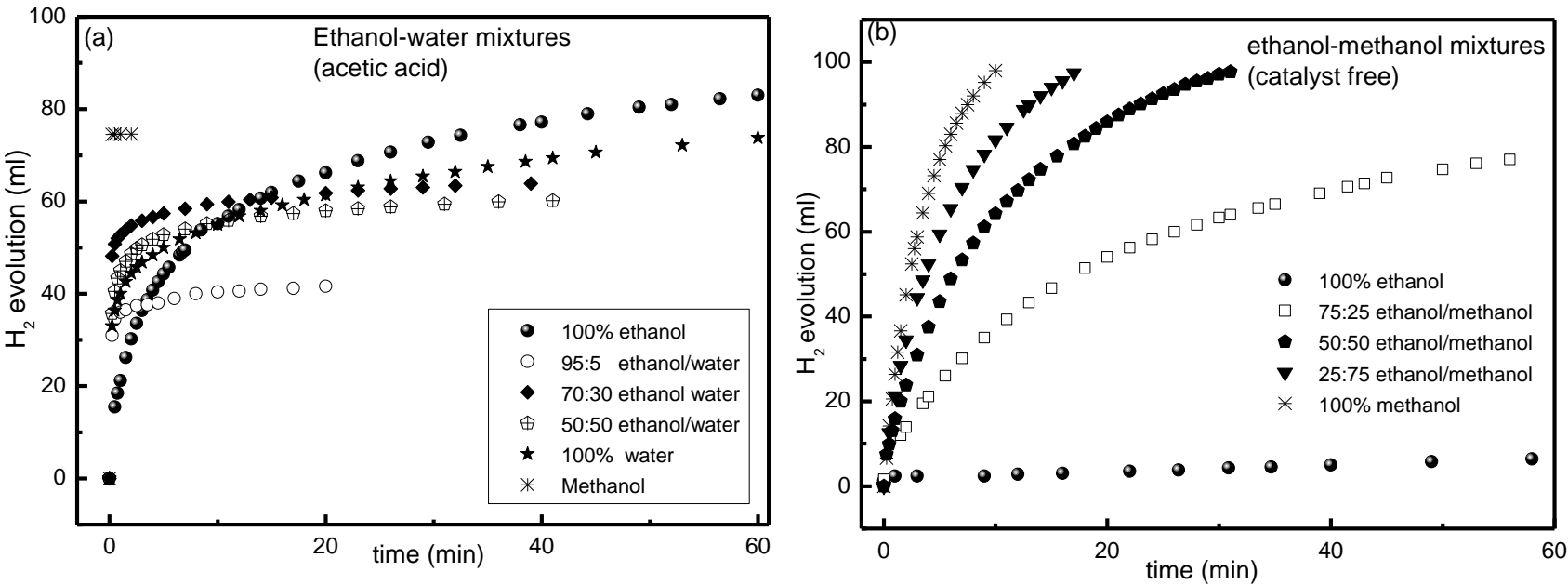
Figure

Figure 3



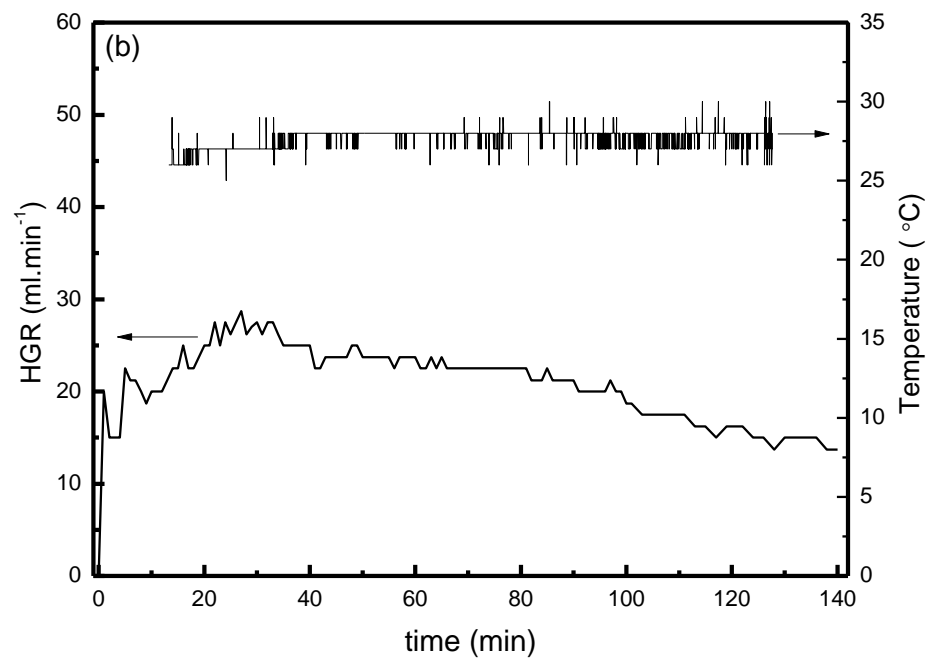
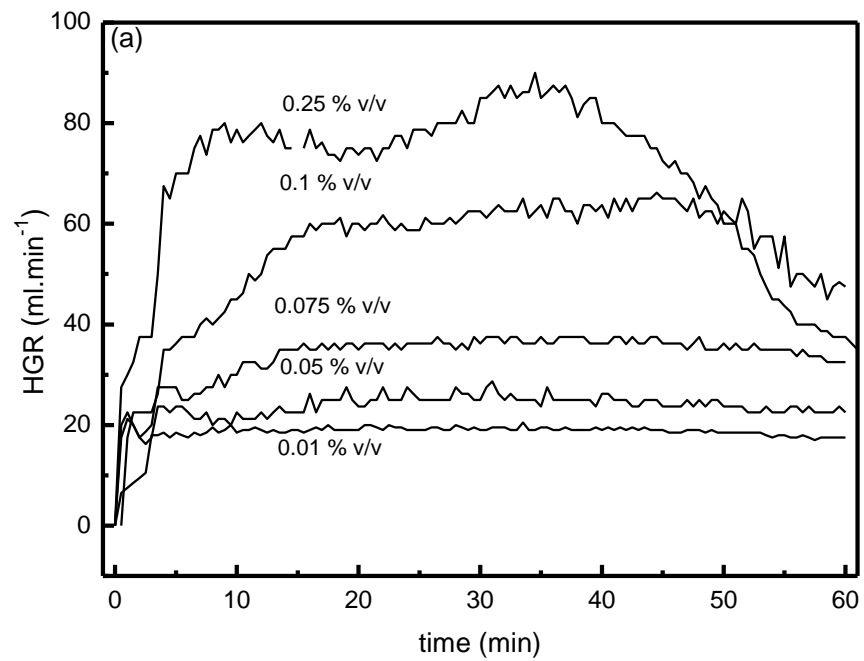
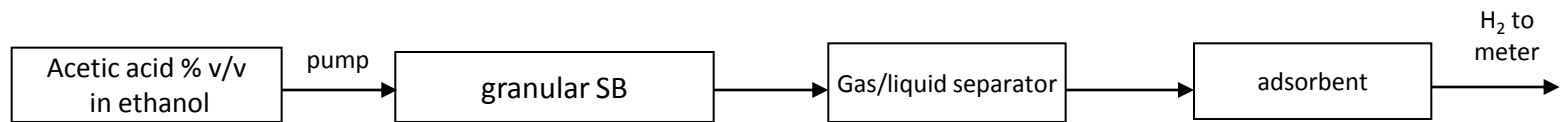
Figure

Figure 4



Figure

Figure 5



Supplementary Material

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